BOB Lime FY Rtc

## **Draft Report**

# Re-equilibration/Corrosion Issues in the Fresno Distribution System

Prepared for:

City of Fresno Water Department

Prepared by:

HDR Engineering, Inc. Fresno, CA

and the

HDR Water Quality and Corrosion Service Laboratory Bellevue, WA

4.3	PH A	AND BLEND Issues	55
4	.3.1	Lead and Copper Surfaces	55
		Iron Surfaces.	
SECTI	ON 5	: RECOMMENDATIONS	56
5.1	PRE-	BLENDING OF SURFACE AND GROUNDWATER IS NOT A REQUIREMENT	56
5.2	Rigo	DROUS PH CONTROL OF TREATED SURFACE WATER IS NECESSARY	56
5.3	ALK	ALINITY AUGMENTATION WOULD ENHANCE PH CONTROL	57
5.4	POL	YPHOSPHATE ADDITION CAPABILITY IS CHEAP INSURANCE	57
REFEI	RENC	ES	58
LIST C	)F AB	BREVIATIONS & ACRONYMS	59

# LIST OF FIGURES

Figure	<u>Title</u>	<u>Page</u>
1-1	One of more than 250 wells that feed the Fresno distribution system	8
1-2	Approximate location on the Enterprise Canal where diversion structure	
	will be placed	9
2-1	Fresno water department personnel retrieving pipe samples	15
2-2	Removing a galvanized pipe sample from West Valley High School	16
2-3	Galvanized pipe sample from Fresno High School	17
2-4	Galvanized pipe sample – 40 years of service	17
2-5	Fresh galvanization layer (75 microns)	18
2-6	Fresno galvanization layer	18
2-7	Iron-oxide accumulation on Fresno galvanized pipe	19
2-8	Iron tuberculation over defects (holidays) on galvanized pipe	20
2-9	Photograph of galvanized pipe section with intact iron-based corrosion scale	21
2-10	Photograph of split galvanized pipe section showing loss of galvanization layer	
	and development of iron-based scale on the steel substrate	22
2-11	Iron/Zinc release pipe loop schematics	23
2-12	Iron release loops in operation	24
2-13	Correlation of apparent color and total iron in stagnant samples	29
2-14	Iron loop data summary – pH effects	
2-15	Zinc loop data summary – pH effects	32
2-16	Iron loop data summary – phosphate effects	33
3-1	Hypothetical polarization curve for a homogeneous metal surface	36
3-2	Potentiodynamic scan on solder surface with fitted theoretical polarization curve	37
3-3	Schematic of the HDR pipe section flow cell (PSFC)	41
3-4	Polarization cell and reticulation loop schematics	43
3-5	LCR recirculation loops in operation	44
3-6	Photo of Fresno copper pipe specimen	46
3-7	Data summary for copper LCR screening	48
3-8	Data summary for Pb/Sn solder LCR screening	49
3-9	Data summary for zinc LCR screening	50
3-10		51
3-11		51
3-12		52
5-1	***************************************	56

# LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
2-1	Composition of a typical Fresno zinc-based scale	20
2-2	Composition of a typical Fresno iron-based scale	21
2-3	Typical source water chemistries	26
2-4	Iron/zinc loop, water quality test matrix	27
3-1	Potentiodynamic scan parameters for metals exposures in Fresno water	39
3-2	Fresno corrosion control strategy testing summary	42
3-3	Fresno pipe section test specimens	44

#### **ACKNOWLEDGEMENTS**

We wish to express our gratitude to the many individuals in the Fresno Water Department who assisted in this project. In particular, we acknowledge the insightful suggestions and comments of Doug Kirk. We wish to thank Martin McIntyre for his technical guidance during the early planning and set-up phase of the project, as well as for his administrative patience in bringing the project to a conclusion. The engineers and scientists at Montgomery-Watson (Walnut Creek, CA), particularly Jim Borchardt and Mark Graham, also provided valuable insights and guidance.

HDR Project Manager was Dave Peterson (HDR - Sacramento). Bench-scale testing was conducted at the HDR Water Quality and Corrosion Services Laboratory in Bellevue, WA, under the direction of Dr. Steve Reiber.

#### **EXECUTIVE SUMMARY**

Replacement or blending of the existing groundwater sources with Enterprise canal water will substantially change the inorganic matrix of the distributed water, and hence, offers the potential for at least a modest re-equilibration of existing corrosion scales. This document presents the methods, results, conclusions and recommendations of the bench-scale iron-release and the Lead and Copper Rule (LCR) screening program conducted as part of re-equilibration/corrosion study for the Fresno Water Department.

Because of increasing demand, the water department is now developing a low-mineral content surface water (Enterprise Canal) as a permanent supply for the Northeastern portion of the Fresno distribution system. Fresno has historically relied on its more than 250 distributed wells tapping a relatively high mineral content groundwater to service its expanding population base. The Enterprise canal will be the City's first surface water source and will, at a minimum, be chemically treated, filtered and disinfected before introduction to the distribution system. This study aims to build consensus in the water department for an acceptable distributed water quality with consideration given to level of treatment, and distribution system effects.

Re-equilibration is the chemical process by which corrosion scales (metal oxides) come to a new thermodynamic equilibrium with a changing water quality. This usually involves solubilization of existing mineral scales and may include a change in oxidation state for some of the metal components. It can lead to a physical weakening of corrosion scales, which in turn makes the scale susceptible to hydraulic scour, flow reversals, and water hammer. The potential water quality impacts of these events relate primarily to increased particulate release (turbidity), potential red water episodes, higher Coliform and HPC counts, and the potential for increased corrosion on the base metal of the pipe wall.

It has been determined that iron release from old, small-diameter, galvanized iron service lines and household plumbing in the Fresno system has the potential to cause some degradation in the aesthetic quality (colored water), but not the safety, of Fresno's distributed water. The primary goal of this re-equilibration/corrosion study is to define those water quality parameters that minimize the potential impact of the new water quality relative to pipe-water interactions in the distribution system and in the customers' homes.

Two forms of testing have been conducted. The first is a comprehensive bench-scale iron release test that utilizes old, small-diameter, galvanized iron service lines obtained directly from the Fresno Water distribution system. These have been placed in pipe loops constructed to simulate a household plumbing system. Varying hydraulic flow regimes, stagnation conditions, blend ratios and corrosion control strategies have been imposed on the pipe loops to assess the impact of different operational and treatment variables. The release of soluble and particulate iron during the stagnation conditions has been used as the principle indicator of potential red water generating conditions. The second testing protocol has concentrated on assessing the potential surface water impacts on lead and copper bearing surfaces in the Fresno distribution system, with

emphasis on ensuring surface water does not generate a compliance issue relative to the Lead and Copper Rule. Again, aged pipe specimens (copper and Pb/Sn solder, and galvanized iron) were taken from the Fresno homes and placed in closed-loop recirculation systems constructed so as to control flow and water quality regimes. A specialized testing procedure using electrochemical corrosion monitoring techniques was used to track and assess corrosion rates on the respective test surfaces.

The most significant results of the combined testing program were:

- Galvanization layers in premise plumbing are still largely intact. Preserving the galvanization layer is the key to minimizing potential red water/aesthetic problem.
- There is a minimal reservoir of iron-based corrosion scales in the Fresno system. Even so, minor red water problems are likely at introduction of treated surface water regardless of blend ratio or corrosion control efforts.
- Zinc layer corrosion is very sensitive to pH. Maintaining a high pH will substantially extend the service life of the existing galvanization layers.
- Blending (TDS content) is important to corrosion on the zinc surfaces, but not as important as pH control.
- Iron release rates from existing scales are not seriously impacted by decreases in mineral content.
- pH is the controlling factor for iron release a full unit decrease can substantially increase Fe release.
- Zinc-orthophosphate addition is not beneficial relative to iron release and red water problems.
- Contrary to Zinc-orthophosphates, polyphosphates offer the potential for enhanced stabilization of iron based scales, and, hence, may be of value during the initial introduction of the surface water.
- TDS variability will not significantly alter metal release ratio on either lead or copper surfaces if pH/alkalinity stability is achieved.
- Lead-bearing solders are sensitive to change in mineral content (blending). However, base corrosion rates are low and the absolute rate remains low even in the face of a large change in mineral content.
- Copper is relatively insensitive to blended waters pH and alkalinity remain important.

The principal recommendations of this report: (1) Pre-blending (ground and surface water prior to distribution) will probably be unnecessary if rigorous pH control is practiced; (2) a finished water pH target of 9.0 is appropriate for the treated surface water; (3) a finished water minimum alkalinity target range of 25 – 30 mg/L (as CaCO<sub>3</sub>) is readily achievable and would substantially improve the buffer intensity of the distributed water, and hence, help to maintain the distributed water target pH; (4) provision for polyphosphate addition will be useful to mitigate potential red water problems and stabilize existing iron-based corrosion scales.

## SECTION 1: INTRODUCTION AND OBJECTIVES

#### 1.1 BACKGROUND

Fresno's existing water source (over 250 deep wells – see Figure 1-1) provides a heavily mineralized water with a moderate concentration of alkalinity and hardness, as well as significant contributions of chloride, sulfate and other inorganic constituents. There is minimal storage within the system, and in most cases the water pumped directly into the distribution grid following chlorination. Although the groundwater is chemically stable relative to calcite precipitation, Lead and Copper Rule (LCR) compliance monitoring has shown the water to be somewhat corrosive to the lead-bearing surfaces in residential plumbing systems. The organic content of the groundwater is low and largely unreactive with chlorine. Hence, the Disinfection By-Product (DBP) formation potential is relatively low, although the presence of bromide assures a broad distribution of DBP species.

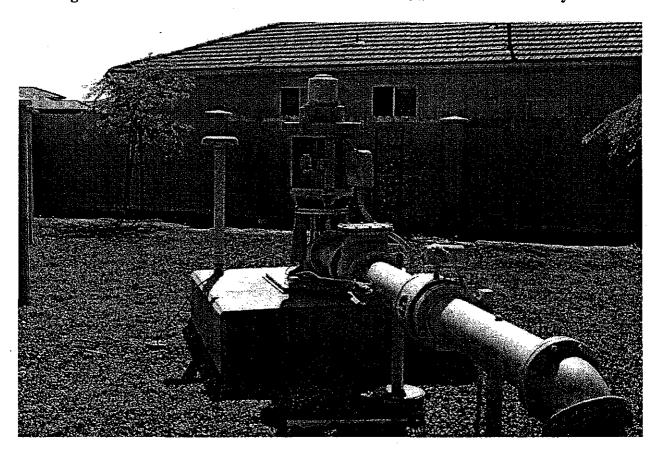


Figure 1-1. One of more than 250 wells that feed the Fresno distribution system.

In 1999 Fresno will begin to import water from the Enterprise Canal (San Joaquin/ Kings River Watershed) to serve as a second water source (Figure 1-2). The raw water from the Enterprise Canal varies substantially from the chemical matrix presented by the historical Groundwater sources. Enterprise Canal water will have a much lower mineral content, including lower buffer capacity, lower overall hardness, and, with some seasonal variation, a lower chloride and sulfate content. Because of the difference in the inorganic character, the potential corrosion impacts of the Enterprise Canal water relative to premise plumbing materials (including galvanized pipe, lead and copper surfaces) and distribution mains were thought to be substantially different from the Groundwater. Hence, the recognition that introduction of a new source requires a review and evaluation of corrosion control strategies for the Fresno system as a whole, including treatment practice and assessment of metal release from existing corrosion scales.

Figure 1-2. Approximate location on the Enterprise Canal where diversion structure will be placed.



The organic content of Enterprise Canal water is moderate to high, variable in concentration and character, and has a high DBP formation potential. Treatability studies to determine enhanced coagulation requirements for the Enterprise Canal water, and blends of Enterprise Canal and Groundwater, have been completed as a part of a different contract and reported in a series of technical memoranda (Enterprise Canal Treatability Studies; Montgomery Watson Engineers – Letter Reports: Dec. 1997, Jan. 1998).

#### 1.2 BLENDING ISSUES

Introduction of Enterprise Canal water to the Fresno system was thought to have the potential to generate several problems relative to corrosion, metal release, overall treatability and aesthetics (taste, odor and color). The more important of these concerns can be described as follows:

**Re-equilibration**. Corroding surfaces on the existing plumbing surfaces have developed corrosion scales that are in equilibrium with the current water quality. These corrosion scales serve to passivate and protect the underlying metal. They also serve as a reservoir of corrosion products (oxidized metals) that can be released when the corrosion scale is forced to equilibrate to a new water quality. Hence, re-equilibration is the chemical process by which corrosion scales (metal oxides) come to a new thermodynamic equilibrium with a changing water quality. This usually involves solubilization of existing mineral scales and may include a change in oxidation state for some of the metal components. It can lead to a physical weakening of corrosion scales, which in turn makes the scale susceptible to hydraulic scour, flow reversals, and water hammer. The potential water quality impacts of these events relate primarily to increased particulate release (turbidity), potential red water episodes, higher coliform and HPC counts, and the potential for increased corrosion on the base metal of the pipe wall. This phenomenon has generated serious consumer dissatisfaction in other communities that have changed the chemical character of their distributed water (i.e. Tucson). It was felt that if not managed properly, this issue could generate consumer complaints within the areas of the Fresno distribution system to receive the Enterprise Canal water.

Because of their volume and friability the corrosion scales of greatest concern are iron-based. Hence, the plumbing surfaces of most concern are distribution mains of unlined cast or ductile iron pipe, and residential plumbing comprised of galvanized pipe. In many cases the galvanization layer will have long since corroded away leaving a mild steel corrosion surface in homes with this plumbing. This type of residential plumbing has generated the most serious re-equilibration problems in other systems, largely because of it proximity to the consumer's tap, and the abundance of iron oxide scales that form on the exposed mild steel surfaces.

Lead and Copper Rule Requirements. Metal release rates on copper and lead bearing surfaces will likely be higher when exposed to the more poorly mineralized blends of Enterprise Canal and Groundwater. pH and alkalinity adjustments may be required to achieve the LCR required "optimal" corrosion control on lead bearing surfaces. Addition of corrosion inhibitors may be appropriate during the period of re-equilibration.

Oscillating Water Quality. As a result of weekly or diurnal variations in demand, portions of the Fresno system may see a variable water quality that oscillates between a low and high mineral content water. The oscillating water quality may be particularly problematic because of the possibility that the unstable mineral content could prevent the effective equilibration and passivation of corrosion surfaces. Hence, portions of the

system may remain at risk for excessive metal release, colored water and other aesthetic concerns for an extended period of time.

#### 1.3 SCOPE AND OBJECTIVES

The study has two principle objectives:

- Determine the potential for serious red water/corrosion problems when the surface water (or surface water ground water blend) are introduced to the Fresno distribution system.
- Define the water quality conditions and blend ratios that can minimize scale or corrosion related problems. Specific water quality/treatment issues to be evaluated included pH and alkalinity effects, blend ratios of Groundwater/Enterprise Canal distributed water, and use of phosphate-based corrosion control agents

Specific work tasks defined in the original contract document included:

- 1. Evaluate iron release rates from existing pipe scales as a function of water quality changes and determine the optimal methods for reducing metal release.
- 2. Determine the impact of possible water quality changes on copper and lead bearing surfaces.
- Evaluate sequestrants as a way of reducing future iron release problems by mobilizing the iron in the existing scales before introduction of the blended water.

It is important to note that, essentially, two different forms of bench-scale testing were conducted as part of this study. The first testing form dealt with issues of iron and zinc release, red water, and the stability of iron based corrosion scales. The second focused on measures of corrosion on the lead and copper bearing surfaces of primary concern to the Lead and Copper Rule. The evaluation of each of these concerns required its own unique testing procedures and protocol. To make the test data and protocols as clear as possible, this report divides the protocol development, testing activities, and data interpretation into individual sections and presents each separately.

## **SECTION 2: CORROSION SCALES AND RED WATER**

#### 2.1 INTRODUCTION

Concerns about structural damage caused by corrosion are common to every use of iron and steel. In drinking water systems, corrosion also causes massive waste of drinking water, accelerates the depletion of disinfectants and impairs the quality of drinking water since even small quantities of iron corrosion products (so called red water) can severely deteriorate its aesthetic properties. Thus, water wastage, substitution of bottled water for tap water, and costs of internal corrosion to cast iron, ductile iron and galvanized pipe are reasons to optimize mitigation measures that minimize corrosion as well as insure the stability of existing corrosion scales. It is also of note that corrosion scales may also shelter harmful bacteria and effect the microbial quality of the distributed water.

Although the species of Fe(II) and Fe(III) are not toxic *per se* and considered as a secondary, non-health related contaminants under the Safe Drinking Water Act, their importance relative to the operation of a water distribution systems and the satisfaction of the customers the systems serves is enormous.

#### 2.2 THEORIES OF IRON CORROSION

Electrochemical oxidation of iron proceeds in two steps, namely  $Fe(0) \rightarrow Fe(II) \rightarrow Fe(III)$ . An electron acceptor is required for each step. In drinking water, oxygen is the typical electron acceptor while chlorine and chloramines are also highly reactive due to their high electrochemical potential ( $E^0_{HCIO/CI} = 1.07 \text{ V}$ , compared with  $E^0_{O,IOH} = 0.27$  at pH 7.0).

Halogenated compounds such as CCl<sub>4</sub> and CHCl<sub>3</sub> have also been found to be active as electron receptors in the oxidation of Fe(0) and Fe(II). The absolute concentrations of these species are much less than those of oxygen or chlorine species, but their electrochemical reactions may significantly affect their fate in potable water distribution networks.

Corrosion causes the formation of exceedingly complex surface scales that include ferrous, ferric and mixed oxyhydroxides, carbonates, phosphates and sulfides [Sontheimer, Kölle and Snoeyink 1981]. Localized electrochemical processes and spatial variations of the composition of iron corrosion products are also notable. The cumulative rate of conversion of  $O_2$  to  $H_2O/OH$ , HClO to  $C\Gamma$  and RX to RH (RX denotes a halogenated organic species) is coupled with the rate of metal oxidation. These processes are expected to balance only at a unique value of the corrosion potential,  $E_{corr}$  [Internal Corrosion 1996], which is amenable to experimental measurements. However, an assumption that  $E_{corr}$  unambiguously describes the state of the iron surface and scales is an over-simplification. The presence of iron minerals that are not good conductors of electricity indicates that reactions of the scales are not governed solely by the  $E_{corr}$  of the metal proper and the corroding surface is subject to both electrochemical and chemical controls. There

are several theories that purport to describe iron corrosion, the formation and release of iron mineral scales, and the production of red water. The most important of these are briefly discussed below:

The Siderite Model. [Sontheimer, Kölle and Snoeyink 1981] suggested that  $Fe(\Pi)$  released by oxidation of Fe(0) forms a dense layer of siderite,  $FeCO_3(s)$ . This layer may be slowly oxidized to a dense protective layer of magnetite,  $Fe_3O_4(s)$ , and goethite,  $\alpha$ -FeOOH(s) pseudomorph. The thin magnetite/goethite layer hinders mass transfer of oxidant to the iron surface. Thus, low corrosion rates can result from relatively high carbonate concentrations and low oxygen, and a pH value that is poised high enough to insure an adequate carbonate concentration and low enough to avoid rapid oxidation of  $Fe(\Pi)$ . The conditions for formation of these protective scales are not completely understood, but they are very important in seeking control strategies by pH and alkalinity adjustment.

Non-Stationary Corrosion and Iron Uptake. [Kuch 1984 and 1988, Kuch and Sontheimer 1986]. Kuch observed that when oxygen in iron pipes was depleted, large amounts of Fe(II) were released suggesting that the corrosion process was continuing]. Lepidocrocite,  $\gamma$ -FeOOH(s), was found to be an efficient electron acceptor in the anoxic oxidation of iron. In this process, iron is oxidized and  $\gamma$ -FeOOH is reduced, both resulting in Fe(II) formation. When oxygenated water mixes with the stagnant water, Fe(II) is oxidized forming red water. The corrosion rate is expected to be insensitive to the oxygen concentration, but iron uptake and red water formation are greatly enhanced by stagnation and oxygen depletion. It was tentatively shown that low pH and higher sulfate promoted the formation of lepidocrocite. Green rusts (Fe(II)/Fe(III) mixed hydroxy carbonates) may also be crucial in the cycling of Fe(II) and Fe(III) during stagnation/re-oxidation periods.

Dispersion and Stabilization of Colloidal Iron. [Olowe and Genin 1991]. An alternative hypothesis for occurrence of red water is tied to colloidal stabilization of iron particulates. In natural waters, hydrous iron oxide particles are virtually always covered by at least a monolayer of natural organic matter (NOM) that imparts a negative charge to their surface thus stabilizing them. In addition, NOM can affect corrosion in a variety of ways. It can reduce Fe(III) to Fe(II) and can form complexes with these ions. NOM adsorbs onto metal surfaces and profoundly affects the morphology of surface scales [Korshin, Perry and Ferguson 1996]. NOM may also interfere in the electrochemical reactions between halogenated species and iron. Despite these effects, no consistent study of NOM effects on the corrosion and uptake of iron has been conducted.

While several attractive hypotheses for iron corrosion and iron uptake exist, they lead to complex, contradictory implications for Fresno water quality mitigation strategies. High pH, low sulfate and high oxygen are needed to avoid Kuch-type iron uptake, but these conditions seem incompatible with the preferred conditions for protective siderite scale formation (lower pH, high  $\mathrm{CO_3}^{2^-}$  and low oxidant concentration). Understanding how to avoid the formation of lepidocrocite and other electroactive Fe oxides, understanding the trade-offs between encouraging siderite formation and discouraging its oxidation appear central to controlling red water.

Many fundamental and practical questions regarding iron corrosion mechanisms and red water formation remain unclear. Some important aspects of the overall iron corrosion process for which we have no satisfactory explanation include:

- Electrochemical Control of Corrosion Reactions: If a thick layer of iron corrosion products is present on an iron surface, is the rate of iron release controlled by changes in the electrical potential of the iron surface (and therefore by water quality factors such as oxidant level (chlorine) that control that potential)?
- Relationship of Scale Properties to Water Quality and Flow Conditions: How rapidly and in what way do the surface properties of the scale change during periods of stagnation, or in response to changes of water quality (e.g., depletion of dissolved oxygen)?
- Mechanisms of Iron Release: Is disaggregation of the accumulated surface scales an
  important source of red water, or is red water primarily or exclusively caused by dissolution
  reactions at the surface, followed by precipitation in solution? What role do specific
  corrosion products play in determining the predominance and rates of the processes? Does
  NOM affect the mechanism of red water?
- Speciation of Released Iron: What iron species are released from the surface? Are they soluble or colloidal? Are they in the +II or +III oxidation state?

By its nature, the study conducted for the City of Fresno cannot answer these fundamental questions. It does, however, give empirical evidence of how some of these factors can impact release of iron from well-acclimated corrosion scales when a major shift in water quality is introduced.

#### 2.3 CORROSION SCALES OF CONCERN

The vast majority of Fresno's distribution system consists of mortar lined ductile iron, PVC, and a limited amount of asbestos cement pipe. Only a small portion of Fresno's distribution system is unlined cast or ductile iron pipe. In short, serious re-equilibration problems related to Fresno's distribution system piping are unlikely.

The corrosion scales of greatest concern in Fresno are those in closest proximity to the consumerthe household plumbing (premise plumbing). In Fresno households, galvanized piping predominates with well over 50 percent of the installation. The next most common premise plumbing material is copper tubing, and although the exact proportion is unknown, local plumbers feel that galvanized plumbing is two to three times more common than copper in older homes. Copper, however, may be more prevalent in some new developments. HDR and Fresno Utility people carried out sampling of pipe materials from households and public facilities in Fresno (see Figures 2-1 and 2-2). Both galvanized and copper pipe samples were collected.

Of most concern was the condition of the galvanized surfaces, which, surprisingly, were found to be in excellent condition. Only a small proportion of the galvanization layer had been lost, and the accumulation of iron-based corrosion scales was minimal on the galvanized surfaces. Figures 2-3 and 2-4 show the exceptionally internal condition of a typical galvanized pipe sample, these samples having been in service for over forty years. The vast majority of galvanized pipe specimens retrieved were in equally good condition. The actual zinc corrosion scale was extremely thin (< 5 mil), somewhat friable, and easily powdered when dry.

Figure 2-1. Fresno water department personnel retrieving pipe samples.

Figure 2-2. Removing a galvanized pipe sample from West Valley High School.

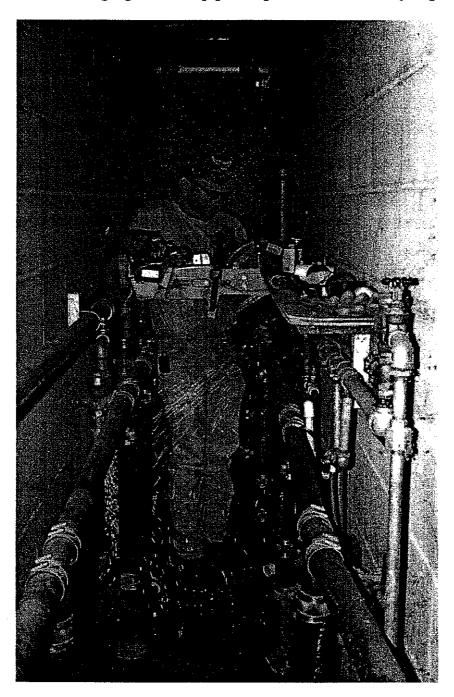


Figure 2-3. Galvanized pipe sample from Fresno High School.

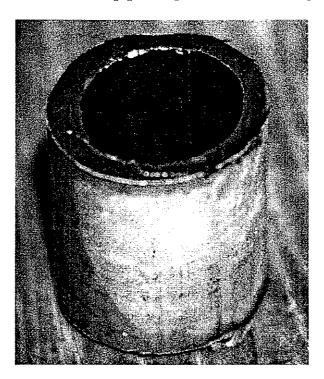
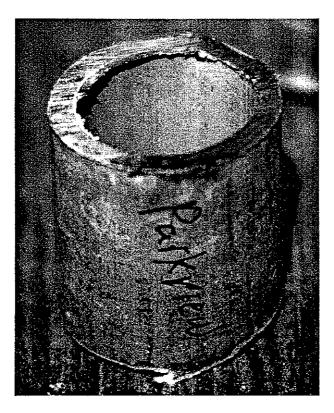


Figure 2-4. Galvanized pipe sample – 40 years of service.



To verify the actual integrity of the galvanization layer, cross-sections of several pipe specimens were polished (300 grit), etched and micrographed. Figure 2-5 shows a fresh galvanization layer with an approximate 75-micron deep layer of zinc. Figure 2-6 shows a Fresno pipe section (>20 years service) with over 40 microns of galvanization remaining. Although we cannot determine what the original depth was on the samples in question, ASTM standards call for a minimum initial galvanization layer thickness of 50 microns.

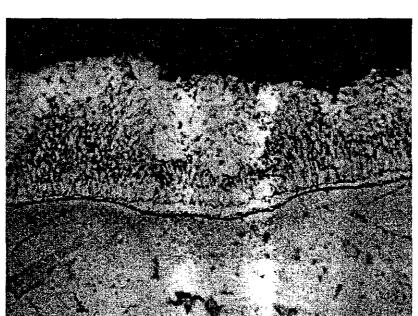
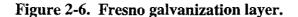
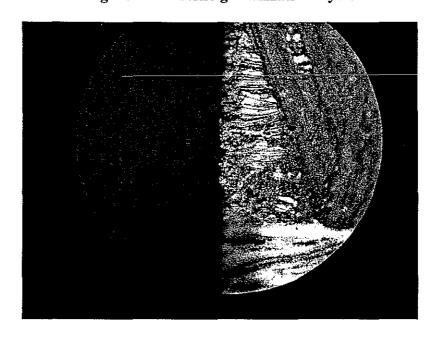


Figure 2-5. Fresh galvanization layer (75 microns).





In only a few circumstance were specimens obtained that showed significant loss of the galvanization layer and the development of meaningful iron-based corrosion scales. Figures 2-7 and 2-8 show the nature of the relatively minimal iron-based scales found in some Fresno pipe samples. In even these circumstances, the galvanization layer below the corrosion scale was largely intact, and the iron tuberculation originated from a small holiday (surface defect) that penetrated the galvanization to the base metal.



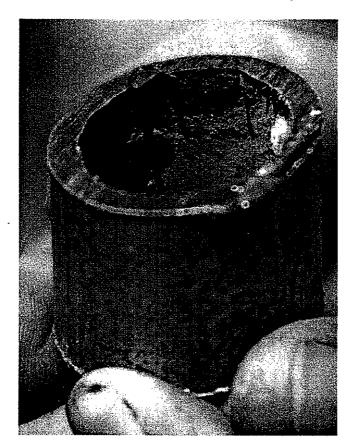
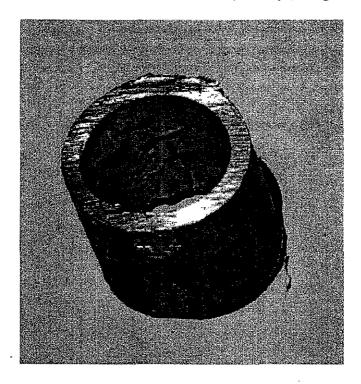


Figure 2-8. Iron tuberculation over defects (holidays) on galvanized pipe.



As a preliminary step in the assessment of metal release and corrosion rates, aged corrosion scales from several Fresno galvanized pipe specimens were extracted and analyzed for both chemical constituents and physical properties. By its nature, this type of analysis is relatively crude and must rely on readily measurable parameters such as hardness, unit mass and analyses of basic chemistry. Because of the amorphous nature of the corrosion scales, it was not possible to identify the precise mineralogy of the scale constituents using X-ray diffraction.

The corrosion scales removed from the pipe specimens were first desiccated, weighed, subjected to fracture analysis, and then dissolved in strong mineral acid. While the composition of the scales showed some variability, analysis of a typical corrosion scale from an intact galvanized iron pipe is shown in Table 2-1. The unit mass of the typical Fresno galvanization layer scale is very low, less than 1 mg/cm<sup>2</sup>.

Table 2-1. Composition of a typical Fresno zinc-based scale (% dry weight).

Zinc oxides	70
Other metal oxides	<10
Carbonates	<5
Silicates	<1
Sand/inorganic sediment	<5
Organic content	<5

There is substantial potential for extended service life of this plumbing material as long as the existing galvanization layer remains intact. The likelihood of a serious red water problem generating from premise plumbing corrosion problems is remote if the galvanization layer is preserved.

The limited amount of iron-based scale on some galvanized pipe samples represents a relatively small reservoir of metals, and is not of itself a re-equilibration concern. The few iron-based scales that were found were soft and friable, with fracture strength less than 50 psi. Figures 2-9 and 2-10 show photographs of a typical iron-based Fresno scale. On a pipe with an iron-based scale the unit mass was generally less than 5 mg/cm<sup>2</sup>. The typical composition of the iron-based scales is shown in Table 2-2 below:

Table 2-2. Composition of a typical Fresno iron-based scale (% dry weight).

Iron oxides	65
Other metal oxides	<15
Carbonates	10
Silicates	<1
Sand/inorganic sediment	5
Total organic/biomass content	5

While the bulk of the scale consists, as expected, of iron oxide related minerals, the scale also incorporates some organic residue (possible biomass) and inorganic particulates (mostly sand).

Figure 2-9. Photograph of galvanized pipe section with intact iron-based corrosion scale.

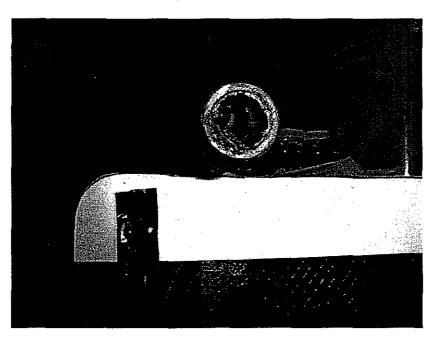


Figure 2-10. Photograph of split galvanized pipe section showing loss of galvanization layer and development of iron-based scale on the steel substrate.



#### 2.4 BENCH-SCALE TESTING APPARATUS

The bench-scale method used in this portion of the study was developed in consultation with Fresno water personnel. This protocol permitted many water qualities to be tested while requiring only a modest amount of distribution system piping and a relatively short testing period.

Closed-loop, fully-recirculating systems were used to implement the iron/zinc release testing. Figure 2-11 schematically illustrates a single, complete loop set-up and labels equipment and flow directions. Eight of these loops were constructed and operated in the HDR Water Quality and Corrosion Services Laboratory in Bellevue WA. Five loops were dedicated to evaluating zinc release form galvanized surfaces, and three were used to examine iron release on lightly to moderately tuberculated pipe sections. Figure 2-12 is a photograph of several loops in operation. The major components of a single loop set-up included:

- One 4' long, 1" diameter iron pipe samples connected in series and vertically mounted.
- Approximately 8 liters of recirculation water (Groundwater or Enterprise Canal water) contained in a covered, high-density polyethylene (HDPE) reservoir.
  - > Initial leaching of plasticizers from the HDPE reservoirs was facilitated by storing water in them for two weeks before filling with the actual test waters.
  - Each reservoir was tapped using a polyvinyl chloride (PVC) bulkhead fitting and outfitted with ball valve to isolate the tank from the pump.

- A 0.25 horsepower, continuous-duty, chemical-resistant, auto-cooled, magnetic-drive recirculation pump.
  - > Pumps were throttled with a PVC discharge needle valve to achieve a target flow rate of 1.0 gallons per minute (equivalent to a flow velocity within the 1" diameter pipe samples of 0.4 feet per second).
  - > Pumps were cycled on and off with automatic timers.
- 1/2" Tygon tubing and 1/2" HDPE barbed tees and elbows to connect tank, pump, and pipe samples.
- Ratchet-style pinch clamps on 3/8" Tygon tubing to serve as air release ports (above the pipe samples) and stagnant water sample ports (below the pipe samples).
- Screw-style pinch clamps before and after each pipe sample to isolate the three pipe sections during collection of stagnant water samples.

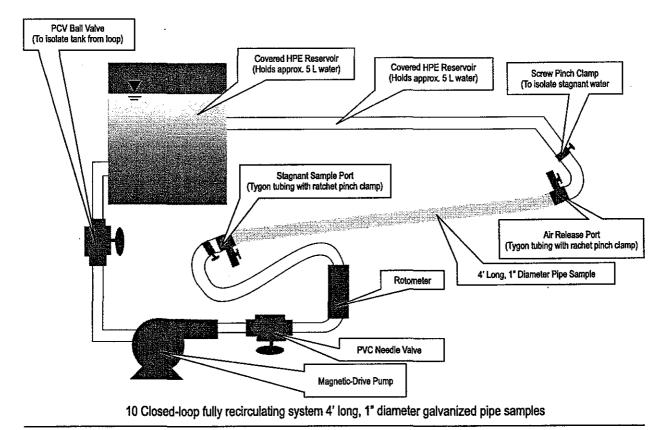


Figure 2-11. Iron/Zinc release pipe loop schematics.

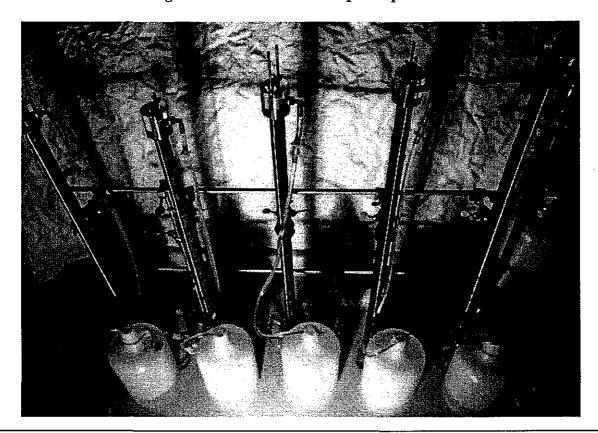


Figure 2-12. Iron release loops in operation.

#### 2.5 PIPE RETRIEVAL AND PRESERVATION

Approximately fifty feet of 1"-diameter galvanized iron pipe was extracted from three different sites in the Fresno distribution system in March 1998. Pipe sections were taken from a High School, a groundwater pumping station, and an apartment complex. In all cases the pipe had been in service for over 20 years, in some cases up to 40 years, and had conveyed only groundwater. The piping was cut into 5' sections in the field, filled with tap water, and shipped to the HDR Laboratory where it was reassembled with compression fittings in its original flow orientation. A continuous flow (0.5 to 1.0 gpm) of dechlorinated treated groundwater was maintained (in the original flow direction) within the pipe until its use in this testing program. Figure 2-12 shows the heavy encrustation of cemented soils and corrosion by-products, which coated some of the retrieved pipe's outer surface. It was necessary to carefully remove much of this debris while preparing pipe samples.

The following steps were taken to prepare the pipe samples for use in bench-scale tests:

• The preserved piping was marked for flow direction and top/bottom orientation.

- Five-inch test segments were cut from the preserved piping using a portable power hacksaw.
- Pipe samples were quickly rinsed of all fresh iron shavings and submerged in tap water to minimize iron contamination and drying of the pipe interior, respectively.
- Pipes were examined and classified. Initially, it was thought that the pipe specimens would be grouped by the degree of inner tuberculation:
  - > Type 1: little internal tuberculation; almost completely smooth, galvanization layer intact;
  - > Type 2: moderate tuberculation covering most of the inner pipe wall;
  - > Type 3: heavy inner tuberculation covering nearly all of the inner pipe wall.
- Pipe cutting, rinsing and classifying continued until enough samples were acquired for all the bench testing. Because the galvanization layer was still intact on almost all the samples examined, the majority met the type one categorization. Only a few specimens rated the type two designations. No samples were characterized as type three. The samples classified as type two were used to evaluate iron release in the dedicated iron loops, while the type one sections were used to evaluate zinc release.
- Pre-cored rubber stoppers outfitted with ½" polyethylene tubing were inserted into each end of the pipe samples. The outer seam between the stoppers and pipe samples was sealed with 5-minute epoxy to ensure water tightness. This method of outfitting the pipe samples virtually eliminated contact between freshly cut iron surfaces and water within the pipe.
- Stoppered pipe samples were linked together with Tygon tubing (maintaining original flow direction and orientation) and placed back in preservation with a continuous flow of dechlorinated tapwater.

After approximately 15 days of preservation, pipe samples were loaded into the test loops.

#### 2.6 TEST WATERS

The basic test waters used in both the Iron/Zinc Pipe Loop testing and the LCR testing were:

- Groundwater from Well No. 177
- Filtered (5 micron glass fiber) Enterprise Canal Water

In both the pipe loop and LCR series of tests it was decided that the principle emphasis would be placed on determining how the variability of the inorganic mineral matrix would impact the iron/zinc metal release and corrosion rates. It was recognized that both parameters would be substantially influenced by the redox conditions (chlorine concentration) in the tests loop, but

that because of the prolonged test duration and periodic stagnation conditions it would not be possible to maintain a stable and consistent chlorine residual. For this reason it was decided to eliminate chlorine as a test parameter and concentrate on the impact of the inorganic matrix. Accordingly, the test waters were dechlorinated before introduction to the test pipes. Dissolved oxygen levels in the loop reservoirs were maintained at saturation conditions.

In order to minimize the potential impact of particulate and colloidal material on the test parameters, raw water from Enterprise Canal was filtered through a coarse glass fiber filter (5 micron) when received at the HDR laboratory. This level of filtration removed some of the turbidity, but little of the true color and none of the dissolved organic matter (DOC).

Water was regularly shipped (usually biweekly) from Fresno via a two-day service. Upon receipt at the HDR laboratory, it was refrigerated until placed in the test loops.

Table 2-3 summarizes the typical water qualities of the two different test waters.

	Groundwater	Filtered Enterprise Canal
PH	7.5 – 8.0	6.5 – 7.5
Total hardness	120 – 140 mg/L	<20 mg/L
Total alkalinity	140 – 160 mg/L	15 – 40 mg/L
Turbidity	<1.0 ntu	>15 ntu
Color	<2.0 pcu	>20 pcu
TOC	<1.0 mg/L	2-8  mg/L

Table 2-3. Typical source water chemistries.

Early in the testing program (March 1998), water was obtained from the Enterprise canal before the seasonal operation of the canal had commenced. The water in the canal at that time consisted largely of agricultural returns and local runoff, with only a small proportion San Joaquin/Kings River Water. The mineral content, as well as color and organic content, of this water was substantially higher (Total Hardness > 50 mg/L; Total Alkalinity > 60 mg/L) than the test water described in the table above. Because it was the only surface water available at the time, the testing program was initiated with this supply and then replaced with lower mineral content canal water when the canal came into operation in April.

#### 2.7 LOOP OPERATION

#### 2.7.1 Testing Duration

Each round of bench-scale testing targeted a specific test water condition and was originally scheduled to last for one week. Once begun, it was quickly realized that in order to achieve stable test conditions and iron/zinc release levels, an extended duration was required. In most cases, this meant a minimum duration of two weeks per round, with some extending to three

weeks. Overall, each test loop underwent at least four different test rounds, for a total test duration exceeding 12 weeks.

#### 2.7.2 Reservoir Water Quality Maintenance

Table 2-4 indicates the targeted water qualities and blend ratios. On nearly a daily basis during both testing rounds, appropriate chemical parameters were measured in each reservoir, chemicals were dosed accordingly to maintain target concentrations (on average), and parameters were remeasured. Flow rate through each loop was measured by rotometer and re-adjusted to within 5% of the 1.0 gpm target value approximately every other day. Temperature was also recorded daily, but not adjusted.

Blend Ratio

Groundwater Enterprise
(100%) 75:25 50:50 25:75 Canal (100%)

High 

Low

X

Х

X

X

 $\mathbf{X}$ 

X

Х

 $\mathbf{X}$ 

Table 2-4. Iron/zinc loop, water quality test matrix.

#### 2.7.3 Iron Stagnation Samples

Zn-PO<sub>4</sub> additive

pH control

Polyphosphate additive

Temperature effects

In Fresno, as elsewhere, the principle location of iron release is the household plumbing systems. The majority of red water complaints relate to iron accumulation that takes place during flow stagnation conditions in the home. To simulate the flow conditions in a household water service line, flow within the bench-scale loops was cycled on and off daily. Water flowed through the loops at a target rate of 1.0 gpm for approximately 16 hours per day. During each night, automatic timers turned the recirculation pumps off for approximately 8 hours. Characterizing water in the pipe samples at the end of this 8-hour stagnant period was a primary focus of the iron release portion of the study.

The following steps were taken to collect stagnant water samples from the individual pipe samples in a loop:

- Screw clamps upstream and downstream of each pipe sample were closed to isolate the pipe samples.
- Any water above the tubing pinch clamp in the air release ports was drained so that it
  would not be collected along with the stagnant sample.

<sup>✓</sup> represents test issue; X represents condition not tested.

- The tubing pinch clamps above and below the pipe samples were opened allowing the stagnant water within the pipe samples to drain into the collection beakers.
- Beakers were covered with laboratory film to prevent contamination between collection and analysis.

#### 2.7.4 Zinc Release Characterization

Unlike iron, zinc release could not be accurately characterized in an overnight stagnation sample. Because of a much slower solubilization rate, it was necessary to measure the total mass of zinc release over a much longer period of time (usually one week). Efforts were made to quantify the different forms of zinc that accumulated in each loop system and it was found that both soluble and particulate/colloidal zinc accumulated at approximately the same rate. The following describes how the different forms of accumulated zinc were quantified in each loop:

- The reservoir water volume on Day 7 was measured to facilitate conversion of total zinc concentration data to total zinc mass values.
- Particles were allowed to settle to the bottom of the reservoir.
- A sample of the settled reservoir water was collected.
- Half of the sample was filtered through a 0.45 μm syringe filter and transferred to an acidified sample bottle for quantification of <u>dissolved zinc</u>.
- The other half of the sample was digested (analogously to digestion of stagnant samples) and transferred to an acidified sample bottle for quantification of <u>colloidal plus dissolved zinc</u>.
- The pipe samples were removed from the loops and replaced with equivalent lengths of polyethylene tubing.
- The reservoirs were acidified to a pH of 2.0 +/- 0.1 using concentrated acid.
- The acidified water was circulated through the loops for two days to promote dissolution of settled particles and metal sorbed to tubing and tank surfaces.
- An acidified water sample was collected from each reservoir after the two-day recirculation period, digested, and transferred to a sample bottle for <u>total zinc</u> quantification.

The soluble and colloidal zinc values were found to be highly variable. It was ultimately determined that the most useful parameter was the total zinc release.

#### 2.8 IRON/ZINC LOOP SCREENING RESULTS

#### 2.8.1 Baseline Conditions

The parameter most useful for characterizing iron release from the different pipe sections proved to be the iron content of the 8-hour stagnation samples taken directly from the pipe sections post-stagnation. The stagnation samples could be easily measured for both total and particulate iron content, and were highly reproducible. Other physical parameters such as color, turbidity and UV-absorbency were evaluated in conjunction with the stagnation iron release, and were found to correlate strongly with the total iron content of the sample. Figure 2-13 shows the correlation of apparent color and the acidified total iron content of a number of different stagnation samples chosen for their distribution of iron levels. Regression analysis indicates a strong correlation, with an R<sup>2</sup> value (correlation coefficient) of approximately 0.8. Similar correlations were observed for turbidity and UV-absorbency.

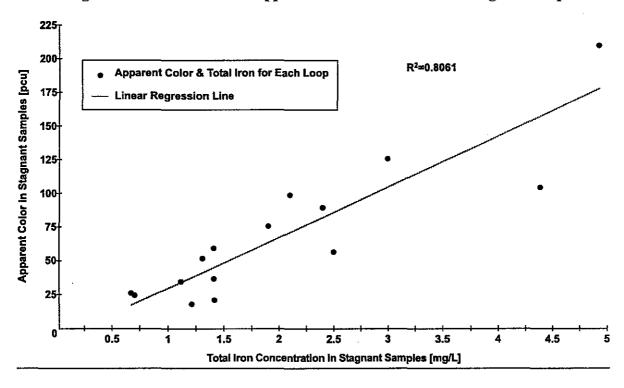


Figure 2-13. Correlation of apparent color and total iron in stagnant samples.

Initially, all iron and zinc loops were exposed (acclimated) to treated Groundwater water for a period of six weeks in order to establish baseline stagnation iron release levels before exposure to any of the test conditions. The reproducibility of stagnation iron release between pipe loops at the end of the acclimation period was generally good, giving specific iron release rates that varied between 3 and 7 mg/M²/day. While baseline iron release showed variability between the different iron test loops, each loop was highly consistent relative to its own release rate towards the end of the acclimation period. Generally, showing no more than a 20 percent day to day variation. The

acclimated specific iron release rate for each loop was the value to which test condition release rates were compared at the end of the respective two-week test cycles.

Because it took nearly a week of exposure to develop meaningful zinc release data, fewer data points are available to determine the acclimated total zinc release. The specific zinc release rates were generally about an order of magnitude lower than for the stagnation iron release measures, varying between 0.1 and 0.5 mg/M²/day. As with the iron loops, the acclimated metal release rate for each loop was the value to which test condition release rates were compared at the end of the respective test cycles.

#### 2.8.2 pH and Blend Effects

Figure 2-14 displays the change in specific iron release (relative to baseline levels) brought about by exposure to different blends of the Enterprise Canal and Fresno Groundwater water at various pH ranges without supplemental alkalinity addition (native alkalinity). The figure also displays the effects of supplemental alkalinity addition where the different source waters and their blend were adjusted to an identical total alkalinity value (sodium bicarbonate addition) to evaluate the stabilizing effects of bicarbonate at a specific pH level.

Interpretation of the results is straightforward. Iron release is sensitive to pH, but largely insensitive to the blend ratio of the water sources or the alkalinity of the water. At pHs substantially lower than the Groundwater baseline level of 7.8, iron release increases significantly. At the low pH (6.0-6.5) iron release is increased by over 40 percent in the unblended Groundwater, and by over 60 percent in the unblended Enterprise Canal water. Conversely, pH levels higher than the baseline level diminished iron release - a pH shift to the range of 9.0-9.5 decreased iron release by as much as 20 percent relative to baseline.

Alkalinity effects on iron release are minimal. In the case of undiluted Enterprise canal water, supplementing the native alkalinity (~20 mg/L as CaCO<sub>3</sub>) with an additional 130 mg/L of alkalinity produced less than a ten percent variation in the baseline level. The impact of alkalinity at both high and low pH was negligible.

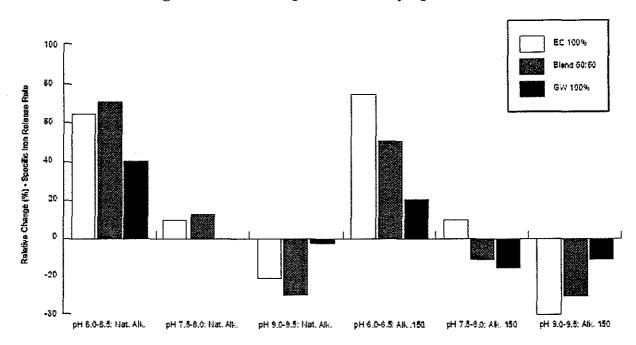


Figure 2-14. Iron loop data summary - pH effects.

The Enterprise Canal and blended water exposures produce changes in iron release that are similar to those observed in undiluted Groundwater. While the blend ratio does not appear to generate a major adverse effect on iron release, it must be recognized that the testing protocol is not sensitive enough to determine more subtle effects. The results do, however, clearly show the sensitivity of iron release to pH, and the importance of maintaining a high pH to minimize iron release.

Similar to Figure 2-14, Figure 2-15 displays the change in specific zinc release (relative to baseline levels) brought about by exposure to different blends of the Enterprise Canal and Fresno Groundwater for various pH ranges at both native alkalinity levels, and with supplemental alkalinity addition. As in the case of iron release, the results clearly demonstrate the sensitivity of the galvanization surface to pH, as well as its relative insensitivity to blending effects and supplemental alkalinity addition. The distinction between the iron and zinc release is in the magnitude of the response. While iron release rates increased by about 50 percent for a 1.5 pH unit decrease, zinc release rates increased by over 200 percent. Zinc release showed little decrease associated with increased pH, but the ability to detect a change is likely hampered by the relatively low baseline zinc release rates and the general imprecision of the measurement technique.

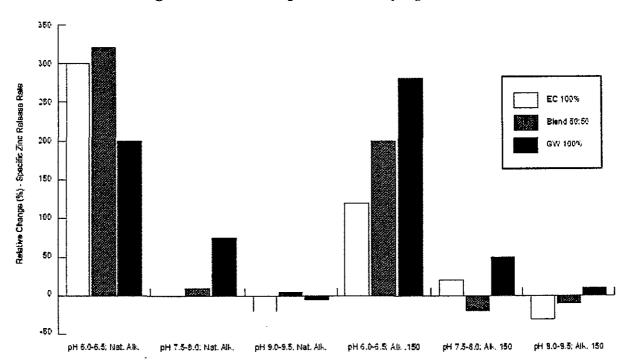


Figure 2-15. Zinc loop data summary - pH effects.

### 2.8.3 Phosphate Effects

Both a pure polyphosphate (Aqua-Mag) and a zinc-orthophosphate formulation were tested relative to their affect on iron release at different dosages and pH levels (Figure 2-16). Because of the need to accentuate difference and acquire data in a short time span, high dosages (up to 25 mg/L as PO<sub>4</sub>) of the formulations were used in the respective pipe loops. In order to more effectively challenge the phosphate formulations, some of the tests were carried out at pH levels lower than baseline.

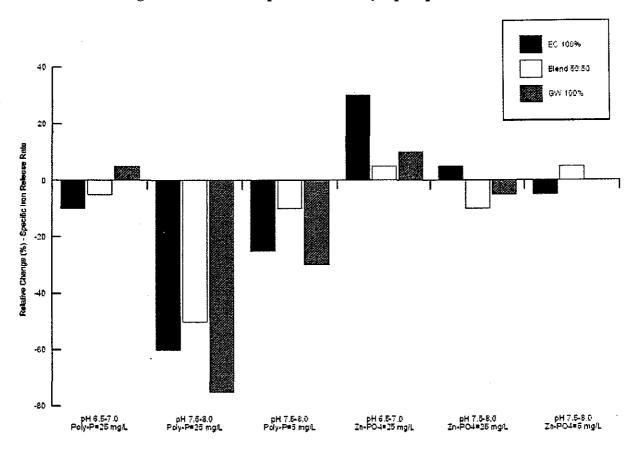


Figure 2-16. Iron loop data summary - phosphate effects.

The results were surprising in that they do not conform to conventional wisdom on the use of polyphosphates. It was originally assumed that the polyphosphate would act as a sequestrant, solubilizing the iron and actually increasing the total iron release. It was though that this might have some operational value for the distribution system if polyphosphates could be used to remove iron tuberculation before the introduction of the Enterprise Canal water. The results indicate the exact opposite. Exposure to the polyphosphate reduces iron release relative to baseline levels. The effect is the same for the undiluted Enterprise Canal water as well as the blend. Moreover, the reductions can be substantial, in excess of 50 percent in the case of an undiluted Groundwater water.

Conventional wisdom was again disappointed relative to the use of zinc-orthophosphate, which was assumed would enhance corrosion scale stability and produce meaningful reductions in iron release - the task for which they are usually marketed,. They did neither. Iron release was largely unaffected by the high concentrations of Zn-PO<sub>4</sub>, although it can be argued that the formulation did prevent an increase in iron release at the lowest pH level tested.

#### SECTION 3: LCR BENCH-SCALE SCREENING

#### 3.1 INTRODUCTION

The City of Fresno has fulfilled its monitoring program requirements relative to the USEPA Lead and Copper Rule (LCR) of 1991. The extensive monitoring required by the LCR has demonstrated that current lead and copper levels at the consumer's tap are well below the LCR action limits. In fact, the difference between the  $90^{th}$  percentile tap water levels for lead and the lead level measured at the source (raw Groundwater water) was less than 5 µg/L. Hence, according to the LCR, corrosion control within the Fresno system is currently "optimized" for lead control.

The optimization requirement for copper is that the 90th percentile tap water level only be less than the action limit of 1.3 mg/L. The 90<sup>th</sup> percentile copper level for Fresno has consistently measured less than 0.5 mg/L.

The blended water LCR screening program described here was designed to provide an indication of the relative effectiveness of various water quality regimens in maintaining "optimal" corrosion control on copper and lead bearing surfaces. The concern being that distribution of the Enterprise Canal water or blends of groundwater and Enterprise Canal water may adversely impact corrosion conditions leading to increased lead or copper release. The screening program employed short-term electrochemical (EC) assessment methodologies focusing on the relationship of water quality to the underlying test specimen corrosion rate. Corrosion rate measurement of this type are sensitive to the variety of physical and chemical parameters that influence the rate of metal oxide generation and metal loss from the corrosion surface. The program yielded several products: (a) the characterization of the initial (baseline) corrosion conditions on the test specimens exposed only to treated Groundwater water; (b) impact of the different blend ratios on the baseline corrosion rates; and (c) effectiveness of the different corrosion control strategies and water quality regimens on each of the material.

Because zinc corrosion (galvanization layers) is of concern for Fresno, galvanized pipe samples were also included in the LCR screening. Zinc corrodes uniformly and can be measured using the same EC techniques used to monitor copper and lead corrosion rates.

It must be stressed that the laboratory procedures used in this program gave only a relative indication of the effectiveness of the different corrosion control strategies at limiting the actual corrosion rates on the specific test materials. Although considerable effort is placed on making laboratory test conditions representative of actual distribution and residential plumbing conditions (i.e., use of plumbing test specimens, test system hydraulics, and water quality maintenance), the water quality variability and physical conditions within a distribution network cannot be duplicated in the laboratory. Caution must be used in extrapolating the laboratory corrosion measures to in-service plumbing and distribution material metal release rates.

#### 3.2 ELECTROCHEMICAL FUNDAMENTALS

#### 3.2.1 The Basics

Corrosion is an electrochemical process, and electrochemistry (EC) can be a powerful tool in its assessment. EC can determine the underlying rate of the corrosion process as well as characterize the surface reactions that control or limit corrosion rates. In the past decade, substantial strides have been made in hardware and technique development. EC methodology has successfully made the evolutionary adaptation from a laboratory oddity to an automated, operational tool useful for screening corrosion inhibitors and optimizing corrosion control strategies.

Unlike weight loss and metal release corrosion methodologies, which are cumulative measures, the EC techniques give a snapshot of the corrosion process. They define the corrosion chemistry at a specific point in time, and hence, are of value in determining how short-term changes in water quality and flow conditions influence corrosion processes.

#### 3.2.2 Polarization Fundamentals

All modern electrochemical corrosion assessment measures rely upon a polarization process. The fundamentals of polarization were defined 50 years ago in the works of Tafel, Butler, Stern and Geary (see References). The principles are straightforward. A measured current is impressed upon a well-defined surface, and the degree to which this current alters (polarizes) the surface potential is measured. The reciprocal relationship between potential and impressed current is obtained for a number of potential offsets (in some cases a continuous scan over a limited anodic and cathodic range). The collected data is interpreted via application of the polarization fundamentals developed by Tafel and Butler.

On a freely corroding homogeneous metal surface, the electron flow generated via oxidation reactions is consumed by adjacent reduction reactions. This characteristic makes it impossible to directly measure the internal rate of electron exchange. Instead, the reaction to an artificial or induced perturbation of the corroding surface, which can be tracked and related to the fundamental internal rate of electron exchange, must be considered. In essence, the test surface is polarized by impressing a current upon it, and the degree to which this shifts the surface potential is measured. By application of EC principles information relative to the freely corroding (unperturbed) current density can be extracted. With the advent of integrated, computer-driven EC systems, the data logging, interpretation, and graphic display functions have been greatly simplified. A hypothetical polarization curve for a homogeneous metal surface is presented in Figure 3-1 along with its interpretation.

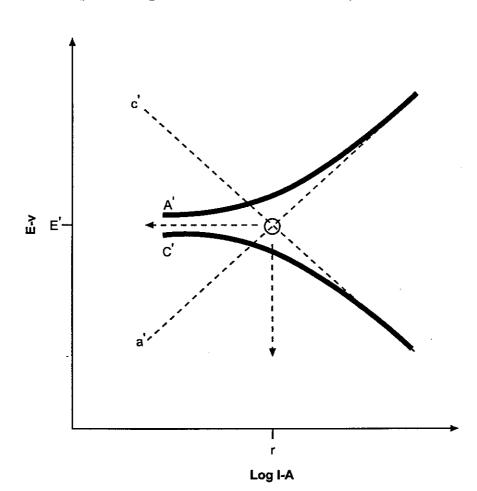


Figure 3-1. Hypothetical polarization curve for a homogeneous metal surface.

The application of a graduated current to the corroding surface produces a characteristic polarization curve from which corrosion rate and electrokinetic information can be obtained.

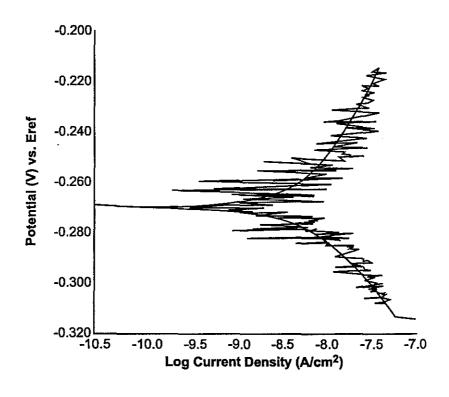
The dashed lines **a'** and **c'** give the partial currents of the respective anodic and cathodic processes (the slope of these polarization curves are termed Tafel slopes). They represent only the current fraction associated with the particular half reaction. The partial currents are not physically measurable and must be inferred from the linear region of the polarization data.

During a potentiodynamic scan, the total anodic/cathodic exchange current is measured (solid lines **A'** and **C'**). These curves represent the sum of the anodic and cathodic partial currents at the indicated potential.

Within any system, the sum of the anodic current exchanges will equal the sum of the cathodic exchanges. For a freely corroding surface, this equivalency is given by the intersection of the anodic and cathodic partial exchange currents (intersection of lines **a**' and **c**'). The intersection defines the corrosion current density (i') of the freely corroding surface, as well as the surface potential of the metal (E').

The most important recent electrochemical advances have been made in interpretive procedures of polarization data. The utility of these procedures lies in their ability to characterize the form of the current-potential curve, with a minimum system perturbation. A number of software packages incorporating regression techniques are available to fit the experimental data to the theoretical equations. These statistical techniques can be applied to very large data sets, substantially improving the characterization of the current-potential curve. Even data sets with a high noise-to-signal ratio can be accurately analyzed. An example of a noisy data set and the theoretically defined polarization curve as calculated using the Gamry polarization analysis software [Gamry Corp. 1992] is illustrated in Figure 3-2. All of the polarization measurements in this study were made using Gamry instrumentation.

Figure 3-2. Potentiodynamic scan on solder surface with fitted theoretical polarization curve.



## 3.2.3 Potentiodynamic Scans

The potentiodynamic scan (PS) was the procedure used in the Fresno study to establish the basic electrochemical parameters and corrosion rates. During the PS, the surface potential of the metal test specimen is forced to move in a continuous sweep from a highly cathodic position (relative to the freely corroding potential) to a highly anodic state. The polarization response of the metal (surface potential versus impressed current) is used to develop a model of the specimen's corrosion behavior.

Since the corrosion current density, i<sub>corr</sub>, cannot be directly measured, it must be estimated from the current versus voltage data. This is done by fitting the measured polarization data to a theoretical

model of the corrosion process. The electrokinetic model of Butler and Volmer is the most generally accepted model of this process [Butler 1924]. It assumes that both the anodic and cathodic processes are controlled by the kinetics of the electron transfer reactions on the metal surface. For a freely corroding homogeneous metal surface, two opposing reactions (the anodic and cathodic exchange reactions) must be considered. The mathematical description of the combination of the cathodic and anodic exchange reactions takes the following form [Stern and Geary 1957]:

```
 \begin{array}{rcl} i = i_{corr} \; (exp. \; (2.3(E-E_{corr})/B_a) \; - \; exp. \; (2.3(E-E_{corr})/B_c) \; ) \\ \\ where \; i & = & measured \; cell \; current \; (Amps) \\ i_{corr} & = & corrosion \; current \; (Amps) \\ E_{corr} & = & corrosion \; potential \; (Volts) \\ B_a & = & anodic \; Tafel \; slope \; (Volts/decade) \\ B_c & = & cathodic \; Tafel \; slope \; (Volts/decade) \\ \end{array}
```

The model predicts that at  $E_{corr}$ , each of the exponential terms equals one, and hence the net overall current is zero and unmeasurable. Slightly removed from  $E_{corr}$ , the anodic and cathodic exchange currents are no longer balanced, and the net exchange becomes measurable. Each of the exponential terms in this region makes a substantial contribution to the overall current flux and must be considered together. Further removed from  $E_{corr}$ , one of the exponential terms predominates and the other term can be ignored. When this occurs, a plot of the log current versus potential (see Figure 3-1) becomes a straight line with a slope equal to the respective Tafel value [Tafel 1904]. The electrokinetic model allows the linear portions of the log current plot to be extrapolated back to their intersection at  $E_{corr}$ . The values of the anodic and cathodic currents are equal at that point and represent the freely corroding current density,  $i_{corr}$ .  $i_{corr}$  is the internal rate of electron exchange between anodic and cathodic sites on the unperturbed surface. The rate of electron exchange can be equated with the conversion rate of metal from an elemental to an oxidized state, and hence can be converted to a mass loss rate. The mass loss rate can then be presented as a penetration rate (milli-inches per year, MPY), which is the convention for reporting corrosion rates in this study.

Therefore, the function of the PS is to generate sufficient data to apply the electrokinetic model and generate the anodic and cathodic electrokinetic constants (Tafel slopes). When coupled with the polarization scan data, these data establish a picture of the electron exchange processes that allows for an accurate estimate of the corrosion current. The important operational parameters for a PS include the scan rate, the maximum potential offset, and the relaxation time between scans. These parameters are specific to the metal specimen and its freely corroding corrosion rate.

#### 3.2.4 EC Limitations

EC applications in water distribution systems are hampered by two confounding physical factors: (1) drinking water is a poor electrolyte; and (2) the application of a perturbation current to a slowly corroding system changes the nature of the corrosion surface.

The poor conductivity of most drinking waters complicates the polarization analysis by adding an uncompensated internal resistance in the surface potential sensing loop. The problem is most

serious at conductivities below 50 microSiemens ( $\mu$ S) and for metals with high corrosion rates. Fresno conductivity's are generally above 100  $\mu$ S, which are acceptable for accurate analysis. The internal resistance (IR drop) distorts the analyst's ability to define the current-potential relationship necessary for an accurate corrosion assessment. Several steps can be taken to limit the IR drop such as, polarization cell geometry and placement of reference electrodes, and cumbersome procedures are available to estimate the IR drop and hence quantitative compensation (i.e., current interrupt).

The second confounding factor represents a more serious analytic problem that is particularly acute in drinking water systems. In some ways, it is analogous to the "uncertainty principle" of quantum mechanics, wherein, by attempting to measure a physical parameter, we unwittingly alter that parameter in ways that are not readily determinable. The application of a polarizing current to a corroding surface unavoidably alters that surface by changing the rate and extent of the respective electronation/deelectronation reactions. Ideally, this alteration remains for only the period of measurement, after which the surface presumably returns to its prepolarized state. However, if the magnitude of the polarizing current is large relative to the extent of the intrinsic corrosion current (freely corroding current density) and its application is extended or repeated, it is likely that the applied current may irreversibly change the surface, possibly by promoting or inhibiting passivation processes.

On a rapidly corroding surface, this is of minimal concern, since even in the short-term the cumulative corrosion current will be orders of magnitude larger than any periodic perturbation current. However, for the minimal corrosion current densities of distribution system surfaces (in the range of 0.01 to 1  $\mu$ A/cm<sup>2</sup>), the perturbation current may be substantial, producing significant surface change, which ultimately invalidates the measure.

Because the Fresno drinking water system corrosion rates are relatively low and the possibility of altering the corrosion surface via the measurement process is substantial, the degree to which the surface potential is shifted during the polarization process must be limited. For the same reason, the scan rates should be as fast as is consistent with accurate characterization of the polarization response. Relaxation time between scans is necessary for the perturbed surface to regain its pre-scan corrosion pseudo-equilibrium. The PS parameters used in the Fresno study are listed in Table 3-1.

Table 3-1. Potentiodynamic scan parameters for metals exposures in Fresno water.

Metal System	Scan Rate (mV/second)	Max. Potential Offset Relative to E <sub>corr</sub> (mV)	Min. Relaxation Time Between Scans (hours)
Copper Alloys	.4	+/-100	6
Lead-Tin Alloys	.2	+/-50	24
Zinc (galv. layer)	.1	+/-200	24

Note: These values assume that substantial passivation of test surface has occurred.

#### 3.2.5 Polarization Cell

Successful EC applications rest on a methodological tripod, two legs of which consist of electronic instrumentation and data interpretation techniques. The third leg is the mechanism and configuration chosen to acquire EC data, the polarization cell. The object of a polarization cell is to isolate the test specimen in such a way as to measure its response to an electrical perturbation, while at the same time maintaining a contact environment that closely replicates the freely corroding conditions of its in-service exposure. Common elements of the polarization cell include a test electrode with well-defined surface area (constructed from the material of interest), a stable reference electrode—against which the electrical response of the test electrode surface is measured, and a counter electrode—used as part of a forcing circuit to induce electrical change on the test surface. The counter electrode is sometimes referred to as the compliance electrode because its voltage relative to the test electrode is monitored and adjusted to produce the desired current flow to/from the test electrode.

The arrangement of these elements and the geometry of the cell are crucial. To minimize internal resistance, the reference electrode must be in close proximity to the test electrode surface. To ensure even current distribution across the test surface, the counter electrode should be equidistant from all points on the test electrode surface. Electrolyte circulation in the cell must be maintained to avoid rate-limiting stagnation conditions and the geometry of the test electrode relative to the electrolyte flow should be representative of in-service hydraulics.

The HDR Pipe Section Flow Cell (PSFC) was specifically designed to make polarization measurements on plumbing materials and uses actual pipe sections as the test electrode [Reiber 1989]. As shown in Figure 3-3, the pipe section is mounted between headpieces, and water flow is channeled through the pipe section bore. Therefore, the polarization cell duplicates both the geometry and hydraulics of an actual pipe. A flexible reference electrode extends from the headpiece and can be positioned to the desired point on the test electrode surface; the counter electrode penetrates the cell axially, and is thus equidistant from all points on the working electrode.

Ag/AgCL Reference Electrode Flow Out Potentiostat Connections **Fritted Junction** Working Electrode (Pipe Segment) Platnum Counter Electrode Flow In

Figure 3-3. Schematic of the HDR pipe section flow cell (PSFC).

The PSFC emphasis on pipe section analysis makes it possible to assess residential and/or distribution plumbing specimens that reflect the true corrosion surface character of in-service pipe. Since the pipe sections are already scaled, prolonged conditioning of the test specimen is no longer required to develop the desired passivation character.

## 3.3 FRESNO TEST PROTOCOL

Fresno and HDR personnel worked together to finalize the screening procedure and select the blend ratios and candidate corrosion control strategies. A total of five control strategies involving multiple inhibitors and water quality regimens were selected. The control strategy tests were carried out using dechlorinated groundwater (see iron release methodology) and filtered water from the Enterprise Canal. This water was shipped on a weekly basis to the HDR Corrosion Services Laboratory. A summary of the testing control strategies, objectives, and test waters is presented in Table 3-2.

Table 3-2. Fresno corrosion control strategy testing summary.

Loop	Control	Test		C1-	Chemical
<u> D</u>	Strategy	Water		Goals	Addition
A	pH and alkalinity adjustment	Treated Groundwater water — dechlorinated	•	Establish plumbing surface pH sensitivity (6.5 – 9.5)  Evaluate the effect of increased alkalinity on copper (blending)	NaOH; H <sub>2</sub> SO <sub>4</sub> ; NaHCO <sub>3</sub>
В	pH and alkalinity adjustment	Filtered Enterprise Canal water	•	Establish plumbing surface pH sensitivity (6.5 – 9.5)	NaOH; H <sub>2</sub> SO <sub>4</sub> ; NaHCO <sub>3</sub>
			•	Evaluate the effect of increased alkalinity on copper (blending)	K <sub>2</sub> HPO <sub>4</sub> ; NaOH; H <sub>2</sub> SO <sub>4</sub>
С	Blending impacts	Treated Groundwater water – dechlorinated and filtered Enterprise Canal water	•	Evaluate three different blend ratios	NaOH; H₂SO₄
D	Blending impacts	Treated Groundwater water – dechlorinated and filtered Enterprise Canal water)	•	Evaluate three different blend ratios	NaOH; H <sub>2</sub> SO <sub>4</sub>
E	pH and ortho- phosphate	Treated Groundwater	•	Assess inhibitory effects	K <sub>2</sub> HPO <sub>4</sub> ; NaOH; H <sub>2</sub> SO <sub>4</sub>
	adjustment	water – dechlorinated and filtered Enterprise Canal water	•	Determine optimal pH range	

The five corrosion testing loops were operated in parallel. Each loop mounted six PSFCs and consisted of a reservoir (4 liters), recirculation pump, rotometer, and throttling valve. A schematic of the test system is shown in Figure 3-4. A photograph of the loops systems in operation in provided in Figure 3-5. Water within the reservoirs was regularly monitored for pH, conductivity and temperature variation and periodically monitored for dissolved oxygen, alkalinity, and inhibitor levels. To maintain the desired water quality and corrosion inhibitor concentrations, the reservoir volume was changed every 48 to 72 hours, which also limited the build-up of metal corrosion products.

Figure 3-4. Polarization cell and reticulation loop schematics.

Copper, zinc, and Pb/Sn solder coupons mounted in individual polarizations cells.

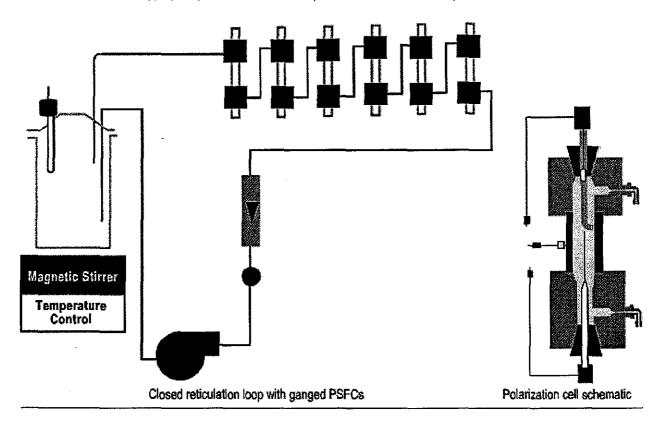
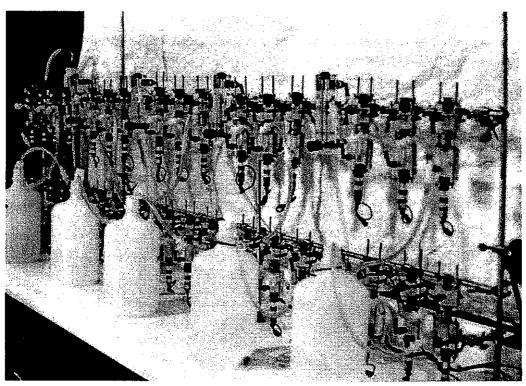


Figure 3-5. LCR recirculation loops in operation.



The specific corrosion materials evaluated in the Fresno screening program included copper and the lead bearing alloys of Pb/Sn Solder and Zinc. Table 3-3 lists the metal type, source and condition of the different test specimens mounted in each of the PSFCs. Each of the five loops contained a replicate of each of the metal types.

Table 3-3. Fresno pipe section test specimens.

Metal Type	Source	Exposure History	Scale Condition	
Copper	3/4" OD Cu residential plumbing	> 20 years	<ul> <li>uniform, adherent</li> <li>greenish-brown scale</li> <li>minimal encrustation</li> <li>cleaned with soft bristle brush</li> <li>no pitting evident</li> </ul>	
Zinc Galv. Layer	Residential tubing	> 25 years	<ul><li>minor degree of tarnish</li><li>little mineral scale accumulation</li></ul>	
Pb/Sn Solder	Fabricated in the HDR Corrosion Laboratory (50% lead, polished to a 300 grit finish)	4-weeks exposure in the laboratory	no visible scale or tarnish present	

For each loop system, the initial specimen exposures consisted of a conditioning sequence in which the pH of the circulating solution was held constant at 8.0 for a period of 10 days before any corrosion rate measurements were taken. The conditioning was performed in the Groundwater baseline water using sulfuric acid and caustic soda as the pH adjustment chemicals. This pH conditioning enhanced the stability of the specimen's electrochemical potential, and improved the reproducibility of subsequent corrosion rate measures.

The basic testing sequence following pH conditioning called for the establishment of baseline corrosion rates on all test specimens prior to the addition of the specified corrosion inhibitor or water quality parameter change. The baseline rates corresponded to the corrosion conditions in the Groundwater baseline waters. A single testing cycle consisted of establishing baseline corrosion rates, imposing the desired chemical or blend ratio change and tracking the change in corrosion rates until stable rates were achieved. A testing cycle was generally two weeks in length, consisting of one week to obtain baseline rates and a second week to assess the impact of the altered chemical regime.

Because there were usually some change or drift in the baseline rates between testing cycles, it was important to establish a new baseline rate on each of the test specimens at the start of a testing sequence. Hence, each testing cycle was self contained and gave an independent assessment of the effect of the particular corrosion control strategy relative to each test specimen's own baseline corrosion rate.

With accommodations for weekends and holidays, corrosion rate analyses were generally made four times weekly on each of the test specimens.

## 3.4 LCR TESTING RESULTS

Data Summaries of the measured corrosion rates (expressed as penetration rates – mils per year (MPY)) and test cycle chemistry is given for each of the material types in Figures 3-7 through 3-12. Because of the number of measurements made on each of the replicate test specimens, and the variability of the measure, the presentation uses bar and whisker plots to present a statistical representation of the test specimen corrosion rates taken after the acclimation cycle. In each of the bar and whisker figures the central point/line represents the median of the post-acclimation corrosion rate measurements made on the test specimen replicates that were representative of the indicated blend/water quality conditions. The spread of the box represents the range of the 75th percentile of all the measurements either side of the average. While the spread of the whiskers represents the 90th percentile range either side of the mean. (A comparison of median values is used to make the assessment of relative control strategy effectiveness.) The observed pH range, blend ratio and other chemical parameters corresponding to each of the test cycles is given in the chemical description at the base of the graph.

#### 3.4.1 Baseline Corrosion Rates

The reproducibility of most corrosion measures in the Fresno tests was good. Corrosion measures on replicate specimens across the five different test loops generally fell within plus or minus 25 percent of each other. In each of the loops, the baseline corrosion rate measurements (pH 7.5 - 7.8) were highly repeatable following the respective test cycles, and the variability of successive corrosion rate measures was minimal. The highest degree of variability was observed on the lead-tin solder specimens but was well within acceptable limits.

Aged copper tubing surfaces in the Fresno system carried a greenish-brown scale indicative of a combination of malachite and cuprite mineral deposits (see Figure 3-6). There was no evidence of pitting on any of the surfaces examined, nor were there visible defects or discontinuities in the scale deposits. Corrosion rates in the respective baseline waters (Groundwater and Enterprise Canal) were low, approximately 0.15 MPY. Although corrosion rate determinations are always a relative assessment, in most residential plumbing systems a moderate copper corrosion rate for copper would be defined as less than 0.2 MPY [AWWA Copper Study Group 1980]. Thus, measured copper corrosion rates on the Fresno specimens indicate they are well passivated and stable. Copper release from these surfaces is relatively minimal, as has been reflected in the LCR compliance monitoring data.

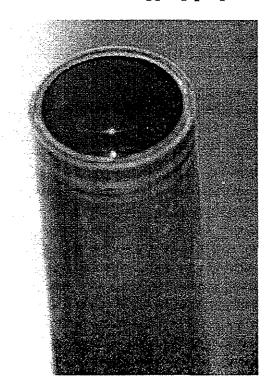


Figure 3-6. Photo of Fresno copper pipe specimen.

The lead-tin solder specimens (laboratory prepared) exposed to the baseline waters did not develop a substantial scale during their approximate 12-week exposure period. The mottled grayish appearance of a well passivated lead-tin solder surface did not appear during the test cycle, and the surfaces remained clean, bright, and only slightly tarnished, as would be expected

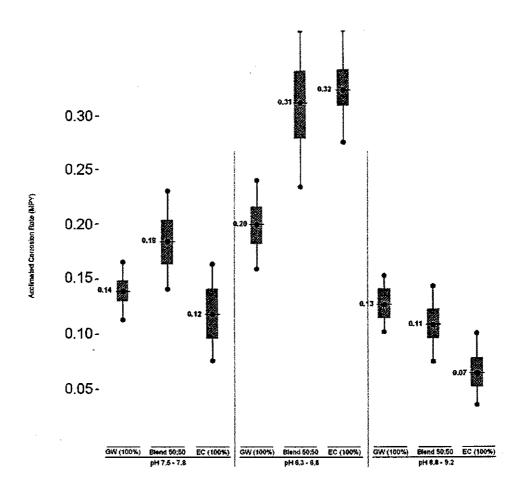
on an unpassivated surface. Even so, the baseline corrosion rate of the lead-tin solder specimens were exceptionally low under almost all conditions - generally less than 0.01 MPY. A moderate corrosion rate for a lead-tin solder surface is less than 0.02 MPY. No evidence was visible that the solder surfaces were shedding lead oxide particulates. Baseline corrosion in the Enterprise Canal water was somewhat higher than the Groundwater, but still low enough as not to be problematic relative to lead release.

Baseline corrosion rates measured on the Fresno zinc samples (aged galvanized pipe) were somewhat less than that measured on the aged copper tubing (0.075 - 0.1 MPY). Unfortunately, the literature provides few references on physical measures of corrosion rates of galvanized surfaces in drinking water environments, hence, it is difficult to verify how the Fresno experience compares to other utilities. However, the fact that Fresno galvanization layers are still intact after 25 years tells us that corrosion rates on zinc surfaces in Fresno groundwater are exceptionally low. The measured baseline rate of 0.075 MPY converts to a loss of approximately 2 microns of galvanization layer per year, or a total of about 50 microns over 25-years. The initial depth of the galvanization on the pipe was approximately 50 - 75 microns, and our investigation of the aged specimens showed that even after 25 years a substantial zinc layer remained. This suggests the measured laboratory corrosion rates are at least consistent with the Fresno experience.

## 3.4.2 pH and Blend Effects

The sensitivity of the test specimens to pH and blending effects was assessed by evaluating corrosion rates at both reduced and elevated pH (relative to baseline conditions) and by comparing the respective source waters and a 50:50 blend of the Groundwater and Enterprise Canal water (Figure 3-7). For copper, the blending studies show that at the nominal baseline pH, the combination of the two waters had little impact on the test specimen corrosion rate. However, a reduction in the pH (6.3 - 6.8) did elevate corrosion rates in all the test waters by as much as 50 percent, while raising the pH of the test waters to about 9.0 had a distinct beneficial impact. Overall, copper corrosion on the Fresno samples was relatively insensitive to changes in alkalinity levels and mineral content produced by the blending. The copper is moderately sensitive to reduced pH, and slightly sensitive to increased pH.

Figure 3-7. Data summary for Copper LCR screening.



Lead-tin solder corrosion rates were also relatively unaffected by the blended water (Figure 3-8). Like copper, a decrease in the pH exposure (6.3-6.8) produced a meaningful increase in corrosion, while an increase in pH (8.8-9.2) produced a decrease of a somewhat smaller magnitude. In general, the observed response of the solder coupon corrosion is of relatively minor consequence since the initial values are so low that modest increases or decreases do not produce a meaningful change in the absolute value of the corrosion rate(or potential lead release).

0.002
0.015
0.015
0.005
0.005
0.005
0.005
0.005

Figure 3-8. Data summary for Pb/Sn Solder LCR screening.

Zinc specimens were not influenced by blending, but were dramatically influenced by decreasing the pH (Figure 3-9). The shift from baseline to the 6.3-6.8 pH range more than doubled the baseline corrosion rate in all the test waters. Increasing the pH, however, did not meaningfully diminish the baseline rate.

GW (100%)

Blend 50:50

pH 6.3 - 6.8

EC (100%)

EC (100%)

These results demonstrate that the corrosion character of all test specimens in the Fresno water were at least somewhat pH sensitive, and generally insensitive to blending of the two baseline waters. In a relative sense, the zinc was most sensitive to pH changes and the copper least sensitive.

GW (100%)

Blend 50:50

pH 7.5 - 7.8

GW (100%)

Blend 50:50

pH 8.8 - 9.2

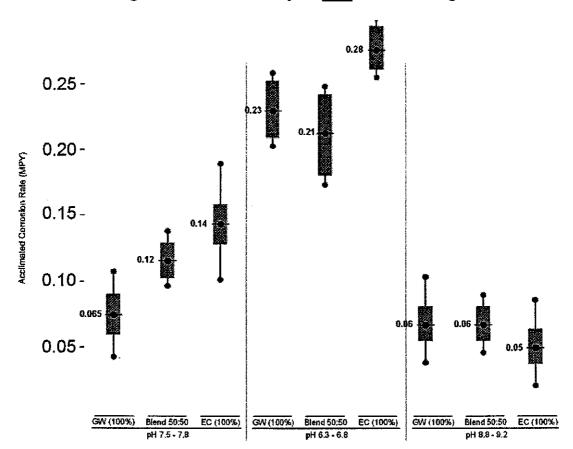


Figure 3-9. Data summary for Zinc LCR screening.

## 3.4.3 Phosphate Inhibitor Effects

The sensitivity of the test specimens to a zinc-orthophosphate inhibitor (Calgon C-9) was evaluated at both baseline and reduced pH, in both undiluted groundwater and undiluted Enterprise Canal water (Figures 3-10, 3-11, and 3-12). Testing was done at the reduced pH to provide an increased challenge to the inhibitor. Results show that corrosion on the aged copper surfaces was barely influenced by the addition of the phosphate, and the lead-tin solder surfaces were similarly unaffected. Galvanized surfaces, however, did derive benefit from the phosphate at the baseline pH, but experienced no benefit at the reduced pH.

Figure 3-10.

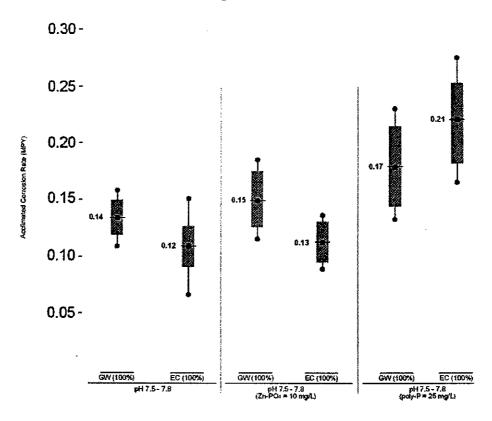


Figure 3-11.

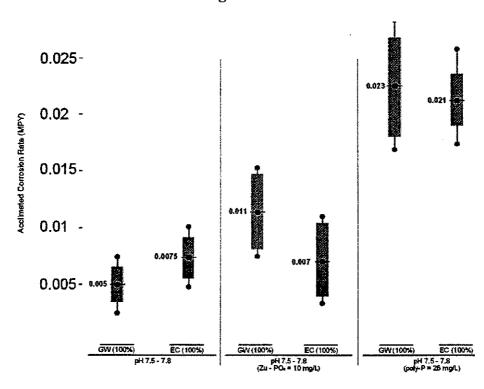
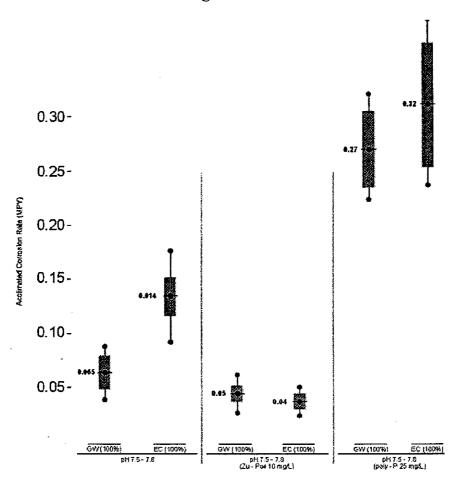


Figure 3-12.



## **SECTION 4: SUMMARY AND CONCLUSIONS**

## 4.1 CORROSION AND SCALE CHARACTER

## 4.1.1 Lead and Copper Surfaces

Baseline corrosion rates measured in Groundwater water are generally low for the LCR test surfaces (aged copper and Pb/Sn solder). Baseline corrosion rates on the Pb/Sn solder surfaces are especially low, well below any level of reasonable concern relative to compliance issues with the LCR. The low baseline corrosion rates are indicative of the historically low metal release levels measured in Fresno's LCR compliance monitoring program. Aged copper corrosion scales are stable and effectively passivate the underlying base metal. The lead-tin solder surfaces did not develop voluminous scales and there was no evidence that the solder surfaces shed lead oxide particulates.

No evidence of pitting was found on any of the Fresno test specimens, nor did any of the corrosion control strategies tested appear to initiate the pitting process on either the aged or fresh specimens. The predominant form of mineral scale present on the copper surfaces was a light greenish-brown deposit, which is typical of a combination malachite and cuprite scale and common to copper surfaces exposed to a groundwater quality of this type.

#### 4.1.2 Iron Surfaces

Iron-based corrosion scales on steel and galvanized pipe surfaces in Fresno homes are relatively soft, somewhat friable, and only partially comprised of iron oxides. While they cover only a minor portion of most galvanized plumbing surfaces, they represent a reservoir of oxidized metal and a source of potential taste and odor related organic material. While relatively small in total mass, the iron scales could be a significant source of iron oxide particulates, and, hence, a potential cause, albeit temporarily, of red water. Destabilizing these scales would have the double impact of generating serious red water complaints, as well as causing a loss of consumer confidence that could jeopardize the long-term success of the new surface water treatment plant.

As in any project of this type, regardless of blend ratio or corrosion control efforts, some minor red water problems, as well as taste and odor complaints, are likely at the first introduction of treated surface water to the Fresno distribution system. If treated appropriately, these impacts will be temporary. The Fresno Water Department should plan on being proactive in its response to the potential complaints. In the best case, this may require a modest public relations effort. In the worst case, the department may need to replace plumbing from some older households that are the most tuberculated.

#### 4.1.3 Zinc Surfaces

Galvanization layers on the majority of Fresno premise plumbing are still largely intact. The baseline groundwater conditions have generated zinc corrosion scales that have remained remarkably stable over several decades. Preserving the existing galvanization layers is the key to minimizing potential long-term red water/aesthetic problem.

### 4.2 ORTHO AND POLYPHOSPHATE EFFECTS

## 4.2.1 Lead and Copper Surfaces

Zinc-orthophosphate was, at best, marginally effective at reducing the corrosion rates on copper and Pb/Sn solder surfaces. The benefits of orthophosphate addition was somewhat apparent at the lower pHs tested (< 7.5), but was not clear at the baseline pH levels assessed. The results of the zinc-orthophosphate testing do not suggest that it would be beneficial to initiate an orthophosphate addition program, nor is there an indication of a need to further control corrosion on these surfaces.

#### 4.2.2 Iron Surfaces

The Fresno tests show that, contrary to anticipation, polyphosphates do not mobilize the metal in the iron-scale, but rather they significantly enhance its stabilization and reduce the rate of iron release. The polyphosphates apparently sorb to the surface of the corrosion scales, slowly hydrolyzing and releasing orthophosphate below the scale surface. The orthophosphate may form precipitation products with metals in the scale that serve to help stabilize the surface, or they may form a ferri-hydroxy-phosphate compound that simply immobilizes iron that might otherwise be release to the water flow. The polyphosphate effect on iron-based scales is not unique to Fresno. Recent studies have shown similar results using corrosion scales generated in other distribution systems.

The results suggests that polyphosphates offer the potential for enhanced stabilization of iron based scales, and, hence, may be of value during the initial introduction of the surface water to the Fresno system. Zinc-orthophosphate addition, however, did not prove to be meaningfully beneficial relative to iron release, even when used at high dosage levels.

#### 4.2.3 Zinc Surfaces

Galvanized surfaces derived modest benefit from orthophosphate addition at the baseline pH, but experienced no benefit at reduced pH.

## 4.3 pH AND BLEND ISSUES

## 4.3.1 Lead and Copper Surfaces

Introduction of appropriately treated Enterprise Canal water, or a blend of treated Groundwater and Enterprise Canal water, is not a threat to the integrity of the existing lead and copper corrosion surfaces, and will generate few, if any, LCR compliance problems. Pb/Sn solder surfaces are the most sensitive to any change in mineral content (surface water addition). However, baseline corrosion rates on these surfaces are so low that the absolute rate remains low even in the face of a large percentage increase.

The pH of the distributed water and maintenance of pH stability are the critical control parameters relative to lead and copper surfaces. The corrosion character of both copper and solder specimens was demonstrated sensitive to a pH reduction. However, as long as a suitable pH control practice is maintained (distributed pH level above 8.5) current corrosion conditions in the distribution system will likely remain unchanged, regardless of surface water addition.

#### 4.3.2 Iron Surfaces

Like the lead and copper surfaces, distribution of treated Enterprise Canal water is not an issue for the iron surfaces. Decreased alkalinity and mineral content of the surface water will minimally impact iron release from existing iron-based scales. Of much greater importance, similar to the lead and copper surfaces, is pH, which appears to be the controlling factor for iron release. A full unit decrease in pH could increase Fe release by as much as 50 percent. Conversely, maintenance of high pH (> 8.5) ensures the stability of the iron-based scale. A high pH policy would, essentially, make the existing iron-based scales "bullet-proof" to water quality variations.

# 504

#### 4.3.3 Zinc Surfaces

Because of the high proportion of Fresno homes with galvanized plumbing, it is critical to ensure the continued integrity of these plumbing systems. Loss of the galvanization layer would substantially increase the long-term possibility of red water and other aesthetic water quality issues.

The zinc-based galvanization layer is very sensitive to pH, more so than any of the other metals tested. This is true both in the sense of metal release from the corrosion scale on the galvanization layer, as well as the actual oxidation processes governing corrosion of the zinc base metal. Maintenance of a high pH in Fresno's distributed water is necessary to extend the service life of the existing galvanization layers.

Blending (TDS content) is somewhat important to corrosion on the zinc surfaces, but not as important as pH control.

## **SECTION 5: RECOMMENDATIONS**

#### 5.1 PRE-BLENDING OF SURFACE AND GROUNDWATER IS NOT A REQUIREMENT

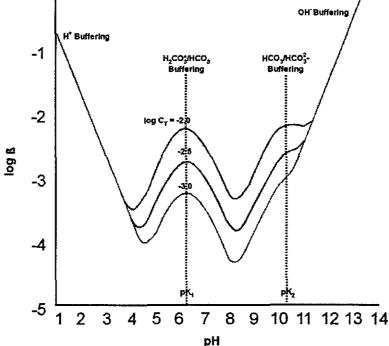
Pre blending (ground and surface water prior to distribution) will probably be unnecessary if rigorous pH control is practiced. While not inconsequential, the potential impacts of distributing an unblended water are not so great as to merit the expense and marginal benefit associated with blending the waters prior to treatment or distribution.

#### RIGOROUS PH CONTROL OF TREATED SURFACE WATER IS NECESSARY 5.2

In the interest of maintaining a stable pH throughout the distribution system, HDR suggests that a permanent finished water pH target of 9.0 be established, and that this level be maintained regardless of the treatment option selected for the Enterprise Canal water. The pH 9.0 target represents a relatively minor chemical cost, but offers the advantage of substantially increased buffering capacity (at pH 9.0 the buffering intensity of the Enterprise Canal is approximately three fold greater than at pH 8.3 - see Figure 5-1). The enhanced buffer intensity will ensure minimal pH drift and variation across the distribution network.

Figure 5-1.

0 H\* Buffering -1 н,созноо, HCO'HCO3-



## 5.3 ALKALINITY AUGMENTATION WOULD ENHANCE PH CONTROL

A finished water minimum alkalinity target range of 30 – 35 mg/L (as CaCO<sub>3</sub>) is readily achievable for Enterprise Canal water and would substantially improve the buffer intensity of the distributed water, and, hence, help to maintain the distributed water pH target.

### 5.4 POLYPHOSPHATE ADDITION CAPABILITY IS CHEAP INSURANCE

In order to mitigate potential red water problems and help stabilize iron-based corrosion, we recommend that the provision for polyphosphate chemical addition be a part of the new surface water treatment plant. We do not anticipate that polyphosphate will be required as a permanent treatment measure, but the results of this study show it can be effective, even as a short-term measure, at enhancing iron-based scale stability and minimizing the potential for red water. In effect, the polyphosphates are an inexpensive form of insurance against potential consumer complaints during the introduction period for the treated surface water.

In the event of a red water episode, the anticipated polyphosphate dosage level could be as high as 5 mg/L (as PO<sub>4</sub>). We do not believe that the selection of the polyphosphate formulation is critical – most polyphosphates are created equal. This leaves the selection open to a bidding process that would minimize cost.

#### REFERENCES

- AWWA Copper Study, 1980, "Internal Corrosion in the Distribution System," AWWA Research Foundation, Denver, 1986.
- Butler, J.A. (1924). "Kinetic Theory of Reversible Oxidation Potentials at Inert Electrodes," Trans. Farady Soc., 19:(729).
- Gamry Corp., 1992, Software Package for Corrosion Analysis, Gamry Corp., Langhorne, PA.
- Internal Corrosion of Water Distribution Systems, 2<sup>nd</sup> edition. American Water Works Association Research Foundation (1996), Denver, CO.
- Korshin, G., S.A.L. Perry, J.F. Ferguson (1996), Influence of NOM on corrosion of copper in potable waters, Journal AWWA, 88:7, 36.
- Kuch, A. (1988). Investigation of the reduction and re-oxidation kinetics of iron (III) oxide scales formed in waters. *Corrosion Science*, 28, 221.
- Kuch, A. (1984). Untersuchungen zum Mechanismus der Aufeisenung in Trinkwasserverteilungssystemen. Dissertation. Universität Karlsruhe.
- Kuch, A., H. Sontheimer (1986). Instationäre Korrosion Eine Ursache der Rostwasserbildung in Wasserverteilungs-netzen. *GWF-Wasser/Abwasser*, **127**, 621.
- Olowe, A.A., P. Bauer, J.M.R. Genin (1989). Moessbauer effect evidence of the existence of green rust 2 transient compound from bacterial corrosion in marine sediments. *Corrosion*, 45, 222.
- Reiber, S.H. (1989). "The Electrochemistry of Copper Plumbing Surfaces," Journal AWWA, 81:(114).
- Sontheimer, H., W. Kölle, V.L. Snoeyink (1981). The Siderite Model of the Formation of Corrosion Resistant Scales, Journal AWWA, 73:11, 572-579.
- Stern, M., A.L. Geary (1957). Journal of Electrochemistry Soc., 104:56.
- Tafel, J. (1904). Z. Physik. Chem., 50:(641).

## LIST OF ABBREVIATIONS & ACRONYMS

AWWA American Water Works Association

EC electrochemistry, electrochemical

EID El Dorado Irrigation District

EPA Environmental Protection Agency

HDR Engineering, Inc.

IR internal resistance

LCR Lead and Copper Rule

μg/L micrograms per liter

μS microSiemens

mg/L milligrams per liter

MPY milli-inches per year

mV milli-volt

PS potentiodynamic scan

PSFC Pipe Section Flow Cell

ZOP zinc-orthophosphate